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(54) Title: ETHYLENE/STYRENE POLYMER SEALANT LAYER FOR USE IN LIQUID PACKAGING		
(57) Abstract <p>This invention relates to the use of a heat sealable multilayer film in manufacturing pouches for containing flowable materials which pouches are in tubular form and have transversely heat sealed ends, said film comprising at least one layer comprising about 10 % by volume of the overall film structure and is made from an ethylene-styrene copolymer obtained using a single site catalyst polymerization process and one or more of the following layers: (a) at least one interpolymers selected from interpolymers of ethylene and one or more C₃-C₂₀ α-olefins made by polymerization processes using single-site catalyst, non-single-site catalyst and mixtures of such catalysts, and blends thereof, said interpolymers having a density in the range of about 0.87 to about 0.940 gm/cc and a melt index of from about 0.2 to about 20 dg/minute and comprising about 10 to about 90 % by volume of the overall film structure; (b) at least one barrier layer selected from nylon polymers comprising about 5 to about 30 % by volume of the overall film structure; polyethylene terephthalate polymers comprising about 5 to about 15 % by volume of the overall film structure; amorphous nylon comprising about 5 to 30 % by volume of the overall structure; ethylene vinyl alcohol comprising about 5 to about 25 % by volume of the overall film structure; (c) at least one tie layer comprising about 5 to about 15 % by volume of the overall film structure and selected from ethylene vinyl acetate polymer, ethylene acid copolymers, ionomers or anhydride functionalized ethylene copolymers; and (d) at least one high pressure ethylene homopolymer.</p>		

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TITLE

Ethylene/Styrene Polymer Sealant Layer For Use in Liquid Packaging

FIELD OF THE INVENTION

This invention relates to the use of a film made from an ethylene/styrene
5 polymer obtained by a single-site catalyst polymerization process, as a sealant
layer in manufacturing packages, in particular, pouches for containing flowable
materials, preferably liquids.

BACKGROUND OF THE INVENTION

Sealing properties of films are key to the effective use of films in many
10 packaging applications. Packaging films include, for example films used to
make fluid containing disposable pouches that may be manufactured on form and
fill equipment employing either impulse or thermic sealing techniques; vacuum
packages for irregular shaped products and for prepared meats, cheeses and the
like; shrink wrapped poultry and skin packaging. While this invention has
15 application to all forms of packaging, it is of particular value in the area of
liquid packaging, namely for the manufacture of pouches for containing flowable
materials.

Packaging machinery is being designed to operate at faster speeds all the
time. The speeds of such machinery demands lower sealing temperatures and
20 hence improved hot tack strength in films to be used to make packaging with
such machines.

Many efforts have been made to improve the sealing properties of films used
in the packaging area, particularly with respect to films used to package flowable
materials. While the advent of single site catalyst polymers or metallocene
25 polymers has provided films of improved hot tack strength, there remains an
ongoing need to improve further the seals of such packages. This is especially
true for film used to make fluid containing pouches, e.g. milk pouches.

Hot tack strength is the ability of a film to seal under stress while still in a
molten state. This property is one of the most critical in packaging applications
30 where machines run at high speeds and sealing takes place between molten
sealing components of a package, thereby placing the sealing components, and

hence the seal under stress when the package is formed, filled and sealed.

It should be noted that in the case of fluid containing pouches made on form, fill and seal equipment, there appears to be a correlation between seal leaker frequency and hot tack strength. This is supported by data gathered in the dairy industry.

The development of single site catalyst (SSC) or metallocene technology has brought about an improved class of polymers ranging from crystalline to elastomeric materials. These polymers have features such as improved impact strength and toughness, better melt characteristics, because of the control over molecular structure, and better clarity. Exxon and Dow have developed SSC or metallocene polymers and each has the benefit of a number of patents relating to these polymers. Exxon is said to use mono- and bis-cyclopentadienyl metallocenes, while Dow's focus is on titanium cyclopentadienyl metallocenes, which it calls "constrained geometry catalysts".

In practice, Exxon produces ethylene-butene and ethylene-hexene polymers, while Dow makes ethylene-octene polymers of the metallocene or SSC type. Dow claims that its metallocene or SSC polymers are different, as they have uniformly introduced comonomers and long chain branching that improve processability in otherwise linear polymers.

BACKGROUND ART

Examples of the polymers of Exxon are found in the following patents and applications, the disclosures of which are incorporated herein by reference: U.S. Patent No. 5,382,630 issued January 17, 1995 to Stehling et al and WO 93/03093 published February 18, 1993 to Meka et al.

Examples of the polymers of Dow are found in the following U.S. patents, the disclosures of which are incorporated herein by reference: U.S. Patents Nos. 5,508,051 issued April 16, 1996 to Falla et al; 5,360,648 issued November 1, 1994 to Falla et al; 5,278,272 issued January 11, 1994 to Lai et al; and 5,272,236 issued December 21, 1993 to Lai et al.

In DUPONT CANADA INC.'s PCT International Publication WO 95/10566 published April 20, 1995, the disclosure of which is incorporated herein by

reference, there are disclosed pouches for flowable materials wherein the sealant film is made from a SSC linear copolymer of ethylene and at least one C_4 - C_{10} α -olefin. Blends of these SSC copolymers with at least one polymer selected from multi site catalyst linear copolymers of ethylene and at least one C_4 - C_{10} α -olefin,
5 a high pressure polyethylene and blends thereof.

In DUPONT CANADA INC.'s PCT International Publication WO 95/21743 published August 17, 1995, the disclosure of which is incorporated herein by reference, there is disclosed an ethylene copolymer film of improved stiffness for use in the manufacture of fluid containing pouches. Typically the structure
10 comprises an interposed layer of polyethylene having a thickness in the range of 5 to 20 microns and a density of at least 0.93 gm/cc and a melt index of from about 1 to 10 dg/minute, the at least one outer layer being a SSC or metallocene polyethylene/ α -olefin film which may have a density in the range of 0.88 to 0.93 gm/cc. The only requirements placed on the stiffening interposed layer are that
15 it be of a particular thickness and density. These are greater in the stiffening layer than in the metallocene or SSC layer(s). This application indicates that the stiffening layer is included in order for the fluid containing pouch to function properly as a pouch from which fluid can be poured when the pouch is placed in a supporting container.

20 DUPONT CANADA INC.'s U.S. Patents Nos. 4,503,102(Mollison) and 4,521,437(Storms), the disclosures of which are incorporated by reference disclose a polyethylene film for use in the manufacture in a form, fill and seal process of a disposable pouch for liquids such as milk. U.S. Patent No. 4,503,102 discloses pouches made from a blend of a linear ethylene copolymer
25 of ethylene and a C_4 - C_{10} α -olefin and an ethylene-vinyl acetate polymer copolymerized from ethylene and vinyl acetate. The linear polyethylene copolymer has a density of from 0.916 to 0.930 g/cm³ and a melt index of from 0.3 to 2.0 g/10 minutes. The ethylene-vinyl acetate polymer has a weight ratio of ethylene to vinyl acetate from 2.2:1 to 24:1 and a melt index of from 0.2 to
30 10 g/10 minutes. The blend disclosed in Mollison U.S. Patent No. 4,503,102

has a weight ratio of linear low density polyethylene to ethylene-vinyl acetate polymer of from 1.2:1 to 24:1. U.S. Patent No. 4,503,102 also discloses multilayer films having as a sealant film the aforementioned blend.

U.S. Patent No. 4,521,437 (Storms) describes pouches made from a sealant
5 film which is from 50 to 100 parts of a linear copolymer of ethylene and octene-1 having a density of from 0.916 to 0.930 g/cm³ and a melt index of 0.3 to 2.0 g/10 minutes and from 0 to 50 parts by weight of at least one polymer selected from the group consisting of a linear copolymer of ethylene and a C₄-C₁₀- α -olefin having a density of from 0.916 to 0.930 g/cm³ and a melt index of from
10 0.3 to 2.0 g/10 minutes, a high-pressure polyethylene having a density of from 0.916 to 0.924 g/cm³ and a melt index of from 1 to 10 g/10 minutes and blends thereof. The sealant film disclosed in U.S. Patent No. 4,521,437 is selected on the basis of providing (a) pouches with an M-test value substantially smaller, at the same film thickness, than that obtained for pouches made with film of a
15 blend of 85 parts of a linear ethylene/butene-1 copolymer having a density of about 0.919 g/cm³ and a melt index of about 0.75 g/10 minutes and 15 parts of a high pressure polyethylene having a density of about 0.918 g/cm³ and a melt index of 8.5 g/10 minutes, or (b) an M(2)-test value of less than about 12%, for pouches having a volume of from greater than 1.3 to 5 litres, or (c) an M(1.3)-
20 test value of less than about 5% for pouches having a volume of from 0.1 to 1.3 litres. The M-, M (2)- and M (1.3)-tests are defined pouch drop tests for U.S. Patent No. 4,521,437. The pouches may also be made from composite films in which the sealant film forms at least the inner layer.

In Falla et al WO 93/02859 published February 18, 1993, the disclosure of
25 which is incorporated herein by reference, there is described the use of metallocene polymers in the manufacture of films used to make fluid containing pouches. These films are characterised as metallocene ultra low density linear polyethylene ("ULDPE") sold commercially as AFFINITY® by Dow and described as a linear copolymer of ethylene with at least one α -olefin having
30 from 3 to 10 carbon atoms, for example, the ULDPE may be selected from ethylene-1-propylene, ethylene-1-butene, ethylene-1-pentene, ethylene-4-methyl-

1-pentene, ethylene-1-hexene, ethylene-1-heptene, ethylene-1-octene and ethylene-1-decene copolymers, preferably ethylene-1-octene copolymer.

In Meka et al WO 93/03093 published February 18, 1993, the disclosure of which is incorporated herein by reference, there are described metallocene
5 polymers useful for making sealed articles, comprising ethylene interpolymers having a CDBI of at least 50% and a narrow molecular weight distribution or a polymer blend comprising a plurality of said ethylene interpolymers as blend components.

Ethylene/styrene polymers can be prepared also using single-site or
10 metallocene polymerization processes. These polymers may be alternating or pseudo-random. Examples of pseudo-random polymers are described in Dow's European Patent Application No. 416,815, the disclosures of which are incorporated herein by reference. Alternating ethylene/styrene copolymers (low styrene content) that have repeat sequences of ethylene/styrene/ethylene may be
15 obtained through catalyst selection (Makromol). Chem., Macromol. Symp. 66, 203-214 (1993), at page 209).

Examples of other types of ethylene/ styrene polymers that are encompassed by this definition include those described in Idemitsu Kosan Co. LTD's Japanese Patent 08020605 A of January 23, 1996.

20 In U.S. Patent No. 5,658,625 issued August 19, 1997 to Bradfute et al, there is described a multilayer film that preferably may comprise outer polypropylene layers between which is an ethylene/styrene layer produced using single-site catalyst polymerization methods. This film is used primarily to produce shrink wrap packaging film.

25 The disclosures of all references mentioned in this description are incorporated herein by reference.

SUMMARY OF THE INVENTION

The present invention provides a sealant film for use in the manufacture of heat sealable film used to make pouches or bags for packaging various products,
30 in particular food products where freshness, cost and film clarity are important properties. Examples are fresh fruits, vegetables and liquids, such as milk and

juice.

In more precise terms, the invention provides a heat sealable multilayer film for use in manufacturing pouches for containing flowable materials wherein the pouches are in tubular form and have transversely heat sealed ends, said film comprising at least one layer comprising about 10% by volume of the overall film structure and is made from an ethylene-styrene copolymer obtained using a single site catalyst polymerization process and one or more of the following layers: (a) at least one interpolymer selected from interpolymers of ethylene and one or more $C_3 - C_{20}$ α -olefins made by polymerization processes using single-site catalyst, non-single-site catalyst and mixtures of such catalysts, and blends thereof, said interpolymers having a density in the range of about 0.87 to about 0.940 gm/cc and a melt index of from about 0.2 to about 20 dg/minute and comprising about 10 to about 90% by volume of the overall film structure; (b) at least one barrier layer selected from nylon polymers comprising about 5 to about 30% by volume of the overall film structure; polyethylene terephthalate polymers comprising about 5 to about 15% by volume of the overall film structure; amorphous nylon comprising about 5 to 30% by volume of the overall structure; ethylene vinyl alcohol comprising about 5 to about 25% by volume of the overall film structure; (c) at least one tie layer comprising about 5 to about 15% by volume of the overall film structure and selected from ethylene vinyl acetate polymer, ethylene acid copolymers, ionomers or anhydride functionalized ethylene copolymers; and (d) at least one high pressure ethylene homopolymer.

Further guidance maybe found as to the amounts and desired properties of these layers from the art and reference may be had to any of the previously mentioned applications and patents in this regard.

As indicated blends of polymers may be used, usually because of processability and/or economic requirements. The blends that may be used herein are any of those which are known in the art and which have been described in any and all of the aforementioned patents and applications.

The ethylene/styrene copolymer layer preferably has a thickness of from

about 25 to about 125 microns. An example of a layer structure for a multilayer film comprises A/B/A layers, where each A layer is an ethylene/styrene copolymer layer and comprises at least 10% by volume of the overall film structure and B is selected from (a) to (d), and comprises about 50% to about 5 80% by volume of the overall film structure.

Another example of a multilayer structure comprises A/B/C/B/A layers wherein layer A is an ethylene/styrene copolymer and comprises at least about 10% by volume of the overall film structure: C is selected from (a), (b) and (d) and comprises about 5% to about 70% by volume of the overall film structure; 10 and B is a co-extrudable adhesive having a thickness comprising about 5 to about 15% by volume of the overall film structure.

The presence of the ethylene/styrene (E/S) copolymer layer provides a film with very low heat seal initiation temperatures. This allows for economies in manufacture of film, packages and bags that can be of importance to food 15 producers. In addition, films made from E/S polymers are stiffer at equivalent heat seal initiation compared to metallocene or Ziegler Natta ethylene/alpha olefin copolymers, and does not pose the handling problems of acid copolymer resins which are often used in these types of film structures. The films are also tough and have good clarity.

20 The sealant film comprises a random copolymer of ethylene and styrene obtained by a single site catalyst polymerization process that may be characterized generally as follows:

density range — about 0.93 to about 1.0 g/cm³;
melting point range — about 136°C(low styrene) to about 50°C (50 wt % 25 styrene) or no melting point at styrene contents above 50 wt %;
melt index— about 0.3 to about 4 gm/10 min at 190°C; and
molecular weight distribution — Mw/Mn about 2.0 to about 4.0 (narrow).

Preferably, the copolymer comprises up to about 40 weight % styrene, most preferably from about 5 to about 40 weight % styrene. It may have a peak

melting point of from about 110 to about 60°C and a melt index that is preferably less than about 4 dg/min.

The sealant film layer is combined with other polymers, copolymers or interpolymers, the choice of which depends upon the intended utility for the final film. The final structure may be obtained by laminating, coextruding or blending. The additional polymers may be made by single site or metallocene catalyst methods of polymerization or by conventional methods, such as those using Zeigler-Natta catalysts or by polymerization methods employing combinations of such catalysts.

When durability is a factor, the film structure may include linear low density polyethylene polymers which are well known in the art and are described in a large number of patents and patent applications, some of which have already been mentioned. Commercial examples of such polymers are Novacor's SCLAIR® 11L4 polyethylene - octene copolymer made by a Zeigler-Natta polymerization process. A commercial example of a suitable metallocene resin is Exxon EXCEED® 350D60 metallocene polyethylene - hexene copolymer.

When an oxygen/flavour barrier layer is required in the structure, a layer or resin that comprises ethylene vinyl alcohol may be used in the film structure. A commercial example of such a resin is EVALCA EVAL® LC-H101. An alternative to this type of material is a polyamide that may be amorphous or crystalline. Commercial examples include DuPont SELAR® PA 3426 an amorphous nylon resin or film or DuPont DARTEK® F101, a nylon 6,6 film, or BASF ULRAMID® B3 nylon 6 film. Another alternative for this type of layer is a polyester film such as that sold by DuPont under the trademark SELAR® PT 8307 or MYLAR® polyester film. Yet another choice of flavour/oxygen barrier is a polyvinylidene chloride, such as that sold commercially under the name MORTON SERFENE® 546 PVDC adhesive.

When the styrene content is high in the sealant layer or film, in a multilayer coextruded structure, it may be necessary to use an adhesive layer to get a functional bond between the ethylene/styrene layer or resin and the other layers.

A suitable adhesive is an anhydride modified ethylene vinyl acetate, a commercial example is DuPont BYNEL[®] 3800 series of co-extrudable adhesives.

5 This invention provides a film structure and a method of making it, as well as packages, preferably pouches for flowable materials, formed therefrom, wherein the sealing properties are substantially increased. By "sealing properties" is meant a substantially increased hot tack strength which is observable in such structures and which therefore allows the production of films and packaging products of greatly increased performance characteristics.

10 Other single site catalyst interpolymers may preferably be selected from interpolymers comprising ethylene and at least one C₄ - C₈ α -olefin, in particular butene, hexene, octene, n-methyl-pentane and combinations thereof. Commercially available polymers include the following: EXACT[®] and EXCEED[®] sold by Exxon and AFFINITY[®] and EPE[®] sold by Dow. The more
15 preferred density ranges for the single-site catalyst interpolymer may be from about 0.910 to about 0.960 gm/cc.

The other layers or resins may be selected, as stated previously from homopolymers, copolymers and terpolymers of ethylene. Especially preferred are interpolymers of ethylene and one or more C₃ - C₂₀ α -olefins, more
20 preferably C₄ - C₁₀, most preferably C₄ - C₆. In particular, butene, hexene, octene and n-methyl-pentane may be selected. Examples of commercially available materials include SCLAIR[®] from Novacor, examples of ultra low density polyethylene materials are ATTANE[®] and DOWLEX[®] from Dow Chemical. However, a wide range of ethylene polymers may be used, with the
25 only criteria being that the layer enhances the hot tack strength of the E/S polymer layer and it meets the intended application requirements. Polymers that fall within this family include both single-site catalyst and multi-site catalyst ethylene polymers and interpolymers, the latter including, for example, Zeigler-Natta catalyst polymers. Also contemplated are hybrid polymers obtained using
30 a process that involves a combination of multi-site and single-site catalysts.

Such polymers are described in US Patent No. 5582923 issued December 10, 1996 to Kale et al, all of the disclosures of which are incorporated herein by reference. This patent describes an ethylene polymer extrusion composition comprising from about 80 to 95 percent, by weight of the total composition, of
5 at least one ethylene/ α -olefin interpolymer composition selected from the group consisting of a homogeneously branched linear ethylene polymer composition and a heterogeneously branched linear ethylene polymer composition, wherein the ethylene/ α -olefin polymer is characterized as having a density in the range of 0.85 g/cc to 0.940 g/cc and from about 5 to 20 percent, by weight of the total
10 composition, of at least one high pressure ethylene polymer characterized as having a melt index, I₂, less than 6.0g/10 minutes, density of at least 0.916 g/cc, a melt strength of at least 9 cN as determined using a Goettfert Rheotens unit at 190°C., a Mw/Mn ratio of at least 7.0 and a bimodal molecular weight distribution as determined by gel permeation chromatography, wherein the
15 ethylene polymer extrusion composition has a melt index, I₂, of at least 1.0 g/10 minutes.

Other examples of these polymers include polyethylene homopolymers made by high pressure processes. Commercial examples include ALATHONTM available from E.I. du Pont de Nemours and ethylene vinyl acetate polymers,
20 examples of which are commercially available from E.I. du Pont de Nemours under the trade-mark ELVAX®.

In another aspect of the invention, there is provided a pouch for containing flowable materials which comprises a film as described previously. The pouch may take the shape of a pillow, which requires support in a container to pour
25 from it or it may be self-standing. In the latter instance, the pouch has a gusseted bottom that allows it to stand. Machines for manufacturing such pouches are well known in the art.

It is possible to use the film of this invention as a sealant film or as a component in a more complex multilayer structure. Typical structures are those
30 known in the art and which will suit the packaging application and still allow the benefits of the enhanced sealing properties of the metallocene or single-site

catalyst ethylene/styrene copolymers.

In another aspect this invention provides a process for making pouches filled with a flowable material, using a vertical form, fill and seal apparatus, in which process each pouch is made from a flat web of film by forming a tubular film
5 therefrom with a longitudinal seal and subsequently flattening the tubular film at a first position and transversely heat sealing said tubular film at the flattened position, filling the tubular film with a predetermined quantity of flowable material above said first position, flattening the tubular film above the predetermined quantity of flowable material at a second position and transversely
10 heat sealing said tubular film at the second position, the improvement comprising making the pouches from a flat web of film comprising a multilayer film as described above.

More preferably, the pouch is sealed through its contents. In addition, the seal is best produced using impulse sealing means.

15 The previously referenced patents and applications describe the various processes that may be used to manufacture the pouches of this invention. Vertical form, fill and seal apparatus is used to make the pouches envisaged herein. A flat web of film is unwound from a roll and formed into a continuous tube in a tube forming section by sealing the longitudinal edges together be
20 either a lap seal or a fin seal. This tube is pulled vertically towards a filling station and is then collapsed across a transverse cross section of the tube, the position of which section coincides with a sealing device below a filling station. A transverse heat seal is made at the section providing an air and liquid tight seal across the tube.

25 The material to be packaged enters the tube above the transverse seal; the tube drops a predetermined distance under the influence of gravity on its load. The sealing device is operated again, and a second transverse seal is made together with a cut through the tube and often through the material placed in the pouch. Thus in this operation, the pouch which has an elongate pillow shape is
30 formed, filled and sealed in a rapid sequence of steps. Many variations of this process are possible and are apparent to those skilled in the art. Examples of

typical liquid packaging apparatus used for this type of manufacture are made by Hayssen, Thimonnier and Prepac.

The term "flowable materials" as used herein encompasses materials which flow under gravity or which may be pumped. Gaseous materials are not included in this definition. The flowable materials include liquids, for example, milk, water, fruit juice, oil; emulsions, for example, ice cream mix and soft margarine; pastes, for example, meat pastes, peanut butter; preservers, for example, jams, pie fillings, marmalade; jellies; doughs; ground meat, for example, sausage meat; powders, for example, gelatine powders, detergents; granular solids, for example, nuts, sugar; and like materials. The pouch of the present invention is particularly useful for liquid foods, for example, milk.

The resins used to make the film of this invention are preferably coextruded in known ways, although other suitable methods may be used, such as those involving laminates, coatings and the like. When blends are used, these may be made by blending the components, prior to or at the time of extrusion, and just prior to remelting in the extruder. A film extruder may be used and the film made using known techniques. An example of a blown film process is found in Canadian Patent No. 460,963 issued November 8, 1949 to Fuller. Canadian Patent No. 893,216 issued February 15, 1972 to Bunga et al describes a preferred method using an external or internal cooling mandrel in the blown film process.

Additives, known to those skilled in the art, such as anti-block agents, slip additives, UV stabilisers, pigments and processing aids may be added to the polymers from which the pouches of the present invention are made. Typically these may comprise up to 5% by weight of total resin components, although as previously indicated, when the additional additives and other components reach this proportion, it is important to be sensitive to the desired hot tack strength enhancement for the structure.

As stated previously, the film of this invention may be used in packaging applications where sealing properties, particularly where hot tack strength is important. Reference may be had to The Wiley Encyclopaedia of Packaging

Technology, 1986, John Wiley & Sons, Inc., under the heading Heat Sealing, the disclosures of which are incorporated herein by reference. Descriptions are found here for all types of heat sealing including bar, band, impulse, wire or knife, ultrasonic, friction, gas, contact, hot melt, pneumatic, dielectric, 5 magnetic, induction, radiant and solvent sealing. Any of these techniques that lend themselves to packaging materials incorporating the film of this invention fall within the scope of this disclosure. Most preferred are pouches made by impulse sealing.

DETAILED DESCRIPTION OF THE INVENTION

10 Some examples of typical film constructions according to the present invention are set out subsequently.

Monolayer Film Structure

A monolayer film may be made from a copolymer of ethylene and styrene (E/S) when high oxygen transmission rates combined with low moisture vapor 15 transmission rates are required, such as for the packaging of fresh fruits and vegetables. An example of such a package would be that used to package prepared salads for sale in supermarkets and similar retail outlets. The film would usually be from about 10 to about 50 microns in thickness. A thicker film would be required for packaging foods with a higher bulk density since these 20 thin films would have insufficient yield strength.

Coextruded Multilayer Film Structure

This structure comprises a three layer film of A/B/A, where A is the E/S copolymer layer which may range from about 5 to about 25 microns in thickness. Layer B may be either of linear low density polyethylene polymer or 25 high density polyethylene ranging in thickness of from about 25 to about 50 microns. This structure has application as a packaging film requiring low heat seal initiation temperature and a high degree of abuse resistance (higher modulus, higher tear strength and hence puncture resistance). The core layer provides these characteristics. When the styrene content is appropriately 30 adjusted, the use of an adhesive layer may be avoided.

Coextruded Multilayer Film Structure

This coextruded five layer film structure comprises A/B/C/B/A, where A is the E/S layer as described above, but the B layers are co-extrudable adhesive, for example BYNEL[®] adhesive, which may be from about 5 to about 15 microns thick. The C layer may be a linear low density polyethylene or high density polyethylene polymer film ranging in thickness of from about 25 to about 50 microns. The C layer may also be an oxygen/flavour barrier layer. As noted above when an oxygen/flavour barrier layer is required in the structure, a layer or resin that comprises ethylene vinyl alcohol may be used in the film structure.

10 A commercial example of such a resin is EVALCA EVAL[®] LC-H101. An alternative to this type of material is a polyamide, which may be amorphous or crystalline. Commercial examples include DuPont SELAR[®] PA 3426 an amorphous nylon resin or film or DuPont DARTEK[®] F101, a nylon 6,6 resin or film, or BASF ULRAMID[®] B3 nylon 6 resin or film. Another alternative for

15 this type of layer is a polyester film or resin such as that sold by DuPont under the trademark SELAR[®] PT 8307 or MYLAR[®] polyester film. Yet another choice of flavour/oxygen barrier is a polyvinylidene chloride, such as that sold commercially under the name MORTON SERFENE[®] 546 PVDC adhesive.

Monolayer Film Structure

20 In this instance, the E/S layer may be laminated to a polyethylene or barrier layer film as described above. The laminating methods are well known in the art and would be apparent to those skilled in the art.

EXAMPLES

The following examples are included to illustrate the present invention.

25 They are not meant to limit the scope of this description or the subsequent claims in any way.

Polymer Sample Preparation

Small samples of ethylene styrene copolymers were prepared in accordance with the methods generally described in Dow's European Patent Application No.

30 0 416 815 A2, the disclosures of which are incorporated herein by reference.

These samples were less than 100-gram samples and were prepared in a small autoclave. All parts and percentages are by weight unless otherwise noted.

Example 1

A one litre Hoke cylinder was charged with toluene (450 ml), styrene (50ml)
5 and polymethyl aluminoxane (PMAO) (4 ml, 7.9 wt% Al in toluene). A second smaller Hoke cylinder was loaded with a 5 ml toluene solution of 0.06 mole of $[(C_5Me_4)Si(Me)_2NC(Me)_3]TiCl_2$. A one litre autoclave was assembled and evacuated. The toluene, styrene, and PMAO solution was added to the autoclave and heated to 90°C. The catalyst solution was added to the autoclave
10 along with 180 psig of ethylene. The polymerization was conducted for 2 hours with the ethylene pressure maintained at 180 psig. The reaction was quenched by addition of 200 ml of MeOH. The precipitated polymer was washed with MeOH, then acetone, and dried to give 59.3 g of white copolymer.

Example 2

15 A one litre Hoke cylinder was charged with toluene (380 ml), styrene (122ml) and PMAO (4 ml, 7.9 wt% Al in toluene). A second smaller Hoke cylinder was loaded with a 5 ml toluene solution of 0.06 mole of $(C_5Me_4)Si(Me)_2NC(Me)_3]TiCl_2$. A one litre autoclave was assembled and evacuated. The toluene, styrene, and PMAO solution was added to the
20 autoclave and heated to 90°C. The catalyst solution was added to the autoclave along with 180 psig of ethylene. The polymerization was conducted for 2 h with the ethylene pressure maintained at 180 psig. The reaction was quenched by addition of 200 ml of MeOH. The precipitated polymer was washed with MeOH, then acetone, and dried to give 21.0 g of white copolymer.

25 Example 3

A one litre Hoke cylinder was charged with toluene (350 ml), styrene (150 ml) and PMAO (4 ml, 7.9 wt% Al in toluene). A second smaller Hoke cylinder was loaded with a 5 ml toluene solution of 0.06 mole of $[(C_5Me_4)Si(Me)_2NC(Me)_3]TiCl_2$. A one litre autoclave was assembled and
30 evacuated. The toluene, styrene and PMAO solution was added to the autoclave and heated to 90 °C. The catalyst solution was added to the autoclave along

with 180 psig of ethylene. The polymerization was conducted for 2 h with the ethylene pressure maintained at 180 psig. The reaction was quenched by addition of 200 ml of MeOH. The precipitated polymer was washed with MeOH, then acetone, and dried to give 53.6 g of white copolymer.

5 Example 4

A one litre Hoke cylinder was charged with toluene (100 ml), styrene (400 ml) and PMAO-IP (3 ml, 9.7 wt% Al in toluene). A second smaller Hoke cylinder was loaded with a 5 ml toluene solution of 0.06 mole of $[(C_5Me_4)Si(Me)_2NC(Me)_3]TiCl_2$. A one litre autoclave was assembled and
10 evacuated. The toluene, styrene, and PMAO solution was added to the autoclave and heated to 90°C. The catalyst solution was added to the autoclave along with 180 psig of ethylene. The polymerization was conducted for 2 h with the ethylene pressure maintained at 180 psig. The reaction was quenched by addition of 200 ml of MeOH. The precipitated polymer was washed with
15 MeOH, then acetone, and dried to give 53.6 g of white copolymer.

Polymer Sample Analysis

The four experimental resin were ground into a coarse powder and then compression moulded into sheets. The compression moulding conditions were as follows: Upper and lower platen temperature had a setpoint temperature of
20 150°C. Thirteen to fifteen grams of ground resin sample was placed between two TEFLON® sheets with a third 0.005" thick TEFLON® sheet with 9.25" by 9.75" opening acting as a frame to contain the sample. The powder was preheat at 150°C for 3 minutes at 1 ton of pressure after which it was pressed for another 4 minutes at 20 tonnes of pressure. After the four minutes the sample
25 was cooled at 36°C per min down to 75°C at which time the press opened and the sample was removed. Generally the samples were 0.009 to 0.012" thick.

For purposes of comparison a commercially available linear low density polyethylene was included in the physical testing. The grade of polyethylene contained nominally 10wt% butene comonomer. Comparative resin sample A
30 (Comp A) was SCLAIR® 8107 polyethylene (sold by Nova Chemicals) was selected because it had a similar melt index to the ethylene styrene copolymers.

Test Results, on two blown film samples made from commercially available polyethylene resins were also included for comparison purposes. The two films were made from a Nova Chemicals, Octene lldpe grade called SCLAIR® 11L4b and a Dow Octene polyethylene plastomer called AFFINITY® PL 1880. The
5 films were blown using a 3/4" diameter, 24/1 L/D extruder with a 1" diameter annular film die and 0.065" die gap. The films were labelled Comp Film B and Comp Film C respectively.

For the experimental resins, two plaques were pressed from each resin sample. The pressed samples were then used to measure the following
10 properties:

Thermal Properties like peak melting temperature (T_m) and enthalpy of melting (ΔH_m) were determined by Differential Scanning Calorimetry according to ASTM D3417. To form a heat seal, it is necessary to bring the contact surface of the seal layer up to it melting temperature and then melt the
15 seal surface. All of the heat required to initiate the seal must be generated by the sealing element. A combination of low melt polymer temperature and low enthalpy of melting would be preferred because in a seal layer it would minimize input demanded of the heating element. The less heat required to melt the seal layer, the less time required to supply the heat from the sealing element and so
20 less time is required to complete the sealing cycle.

Summary of Test Method

This test method consists of heating or cooling the test material at a controlled rate in a controlled atmosphere and comparing the areas under the crystallization exotherm or fusion endotherm of the test material against the
25 respective areas obtained by the similar treatment of a well-characterized standard.

Tear Resistance Properties or "Elmendorf Tear" were measured according to ASTM D1922. The Elmendorf Tear value is used to estimate a films resistance to propagating a tear. In the test, the film is intentionally
30 notched to initiate the place on the film where tearing will occur. The test then measures the difficulty to continue or propagate the tear. In a form/fill/seal

package like the liquid pouch, the cut-through horizontal seal area often has notches or nicks left in the film from which tears will propagate during handling and or shipping. The Elmendorf Tear test is a useful predictor of how well the area of horizontal seal (which is a cut through seal) will stand up to this abuse.

- 5 Higher Elmendorf Tear values are preferred.

Summary of Test Method

The force in grams required to propagate tearing across a film or sheeting specimen is measured using a precisely calibrated pendulum device. Acting by gravity, the pendulum swings through an arc, tearing the specimen from a precut
10 slit. The specimen is held on one side by the pendulum and on the other side by a stationary member. The loss in energy by the pendulum is indicated by a pointer. The scale indication is a function of the force required to tear the specimen.

- Density by Buoyancy Displacement** was measured according to ASTM
15 D792. For polymers synthesized from the same monomers, density is a useful predictor of monomer concentration. In the case of an ethylene styrene copolymer, density increases with increasing styrene content.

Summary of Test Method

- Determine the mass of a specimen of the solid plastic in air. It is then
20 immersed in a liquid, its apparent mass upon immersion is determined, and its specific gravity (relative density) calculated.

- Tensile properties** at 20"/min XHS, including Tensile Yield, Yield at Break, Elongation at Break and 2% Secant Modulus were determined according to ASTM D882. Tensile properties predict toughness and stiffness of the
25 polymer. For a seal layer, the seal must have sufficient strength to resist bursting during the manufacture and filling of the package and downstream abuse. The three values of tensile yield, yield at break and elongation at break predict the toughness of the seal area. Having high tensile yield and high yield at break without a good elongation (preferred +400%) is not a sufficient condition
30 for a good seal layer. Low elongation values indicate the polymer would fail in a brittle mode when the seal layer is stressed. High tensile yield values are

generally preferred because the film can be pulled at higher speeds (which induces more film tension) without undesirable stretching of the film. Also a higher tensile yield gives the package better burst strength. The secant modulus, is a reflection of film stiffness. A stiffer film can allow down gauging in some applications.

Summary of Test Method

A rectangular shaped piece of film 1 inch wide and 6 inches long is gripped at each end, the grips are separated by 4 inches. At the start of the test, one grip moves away from the other stationary grip at a constant speed of 20 inches per minute. The resistance or force applied to the grip by the film, is measured continuously as a function of the displacement of the jaw, from the start of the test until the film breaks (test end). By analyzing the graph of force vs. displacement, Tensile Yield, Yield at Break, Elongation at Break and 2% Secant Modulus for the test film can be calculated.

Melt Index at 190°C and 2.160 kg load was measured according to ASTM D1238. Melt index is commonly used in the plastics industry to estimate the rheological properties of the polymer melt. That is, how the polymer will respond to the stresses induced by melting the polymer, pumping the polymer and then blowing the polymer into a thin film. In the melt index test, the resistance of the molten polymer to flow is measured under a constant stress. Polymers with very little resistance to flow have high melt indices. Polymers with a low of resistance to flow have low melt indices. For polymers that will be used to extrusion blow thin films, melt indices in the 1.0 range are commonly used with polydispersity indices from 2 to 5. When the melt index drops below 0.5, the film will have surface roughening, sometimes called "melt fracture". The melt fracture reduces the clarity of the film and ease of heat sealing. When the melt index is greater than 5, there may be problems with establishing and maintaining a uniform film gauge around the process.

Summary of Test Method

Melt Index was measured at 190°C with a 2.160 kg. load. In this test, a plunger pushes the molten polymer through a capillary die under a constant load

(force). After the plunger has travelled a specified distance under constant load, the rate of polymer extrusion from the die is determined. The rate of flow (in grams/10 minutes) is reported at the melt index.

The **Kayeness Melt Viscosity** was measured at 190°C and 46/s shear rate using a 15/1 L/D orifice with a 0.04" diameter opening according to ASTM procedure D3835. Kayeness viscosity is a more elaborate predictor of polymer rheology compared to a melt index test. In this test the polymer is subjected to four different shear rates and an estimate of the polymer melt viscosity at each shear rate is measured. An ideal polymer for extrusion blowing into a thin film would have a very large viscosity or resistance to flow at low shear rates. This is because low shear is typical of the polymer melt just as it exits the die. Conversely at the relatively high shear rates encountered in the feed and transition section of the extruder that melts and pumps the polymer, the polymer viscosity should be as low as possible to minimize power consumption.

15 **Summary of Test Method**

Kayeness Melt Viscosity was measured at 190°C and 46/s shear rate using a 15/1 L/D orifice with a 0.04 inch diameter opening according to ASTM procedure D3835. In the Kayeness viscosity test, a plunger pushes the molten polymer through a capillary die at several pre-selected speeds. The speed, at which the plunger pushes the polymer through the capillary die, is used to estimate the shear rate at the wall of the capillary. The force required to maintain the plunger at that constant speed is continuously recorded and can be used to calculate the shear stress and apparent melt viscosity at the specified melt temperature and shear rate.

25 **Styrene content** in each sample was determined by Proton Nuclear Magnetic Resonance (H+ NMR).

TEST RESULTS

TABLE I FILM SAMPLES PREPARED				
			Frame	platen 1-2
Example	Resin	Shot size	Opening	Setpoint
Comp Film A1	Comp A	13.2	9" x 9½"	150°C
Comp Film A2	Comp A	13.6	9" x 9½"	150°C
Film 1-1	1	13.2	9" x 9½"	150°C
Film 1-2	1	14.2	9" x 9½"	150°C
Film 2	2	12.0	9" x 9½"	150°C
Film 3-1	3	13.7	9" x 9½"	150°C
Film 3-2	3	13.8	9" x 9½"	150°C
Film 3-3	3	13.0	9" x 9½"	150°C
Film 4-1	4	14.4	9" x 9½"	150°C
Film 4-2	4	15.6	9" x 9½"	150°C

TABLE II		
THERMAL ANALYSIS OF FILM SAMPLES		
	Tm	ΔH_m
Example	°C	J/g
Film 4-1	90	0
Film 3-2	102	65
Film 2	106	81
Film 1-1	119	135
Comp Film B	101	57
Comp Film C	126	106

TABLE III
TENSILE PROPERTIES OF FILM SAMPLES

SAMPLE	YIELD PSI	STRESS AT BREAK PSI	ELONGATION AT BREAK %	SECANT MODULUS PSI	GAUGE MILS
Comp Film A2	1892	1500	460	35951	9.1
Film 1-2	2345	843	40	39857	10
Film 2	1453	794	136	29322	10
Film 3-3	1333	2515	552	15899	9
Film 4-2	1221	1213	98	15923	12
Comp Film B Machine Direction	1422	3626	675	23854	3.0
Comp Film B Transverse Direction	1191	3388	725	24021	3.0
Comp Film C Machine Direction	650	3656	629	6380	3.4
Comp Film C Transverse Direction	850	4556	687	6650	3.3

TABLE IV ANALYSIS FOR STYRENE CONTENT PROTON NMR	
Sample	mol% styrene (wt% styrene)
Film 1-1	2 (7)
Film 2	7 (22)
Film 3-1	8 (24)
Film 4-1	28 (59)

TABLE V TEST RESULTS FOR MELT INDEX, DENSITY, KAYENESS MELT VISCOSITY AND ELMENDORF TEAR KAYENESS MELT VISCOSITY (Pas) AT 190°C							
Film Sample	MI @190°	Density (gm/cm ³)	47/s	281/s	562/s	937/s	Elm. Tear (gm/mil)
Film 4-2	1.203	1.000	1561	504	330	247	37
Film 4-1	1.255	1.04	1563	541	347	248	47
Film 3-2	4.201	0.956	1080	522	375	284	547
Film 3-3	4.255	0.950	1087	522	374	283	552
Film 3-1	4.250	0.949	1060	508	369	281	540
Film 2	4.831	0.963	930	442	323	242	502
Film 1-1	2.004	0.939	1244	484	329	247	91
Film 1-2	1.888	0.940	1209	493	341	255	100
Comp Film A-1	4.931	0.919	1041	471	353	281	40
Comp Film A2	4.948	0.930	1459	485	356	279	59
Comp Film B	.662	.918					482 MD 660 TD
Comp Film C	1.21	.902					246 MD 471 TD

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings that are used to illustrate the invention

Figure 1 is a representation of a plot of moles of styrene, final melting point of the films tested and Hm (endotherm on melting);

5 Figure 2 is a representation of a plot of Elmendorf Tear, final melting point of the films tested and tensile elongation; and

Figure 3 is a representation of a plot of Secant Modulus and final melting point of the films tested.

DETAILED DESCRIPTION OF THE DRAWINGS**10 Preferred Composition for Seal Layer**

Considering only the requirement that the seal layer form a seal at the lowest possible sealing bar temperatures then it would be preferred to have the melting point of the seal layer as low as possible and to have the size of the endotherm on melting as small as possible. From Figure 1, it is apparent both the melting
15 point and the size of the endotherm are minimized by increasing the styrene content in an ethylene styrene copolymer.

However, it is also preferred to have Elmendorf Tear Strength as high as possible to prevent bursting or tearing of the package during distribution. Similarly, it would be preferred to have the tensile elongation as high as possible
20 to maximize the toughness of the seal and package.

In Figure 2, the Elmendorf Tear resistance was maximized at ethylene/styrene melting points in the range of 100°C to 110°C. Those melting points corresponded to styrene contents of 6 to 10 mol% styrene (20 to 30 wt% styrene).

25 Relative to commercially available polyethylene and polyethylene plastomers represented by Comp film B and Comp film C, the ethylene styrene polymers containing 7 and 8 mole percent styrene had a superior balance of low heat seal initiation (as measured by melting point and size of melting endotherm) and toughness (Elmendorf Tear resistance).

30 Specifically, films made from Examples 2 and 3 had low melting points 106°C and 102°C, respectively, and melting endotherms of 81 and 65 J/g.

These ethylene styrene thermal properties are lower than Comp Film B and similar to Comp Film C. The tear properties on films made from Examples 2 and 3 were comparable to the tear properties of Comp Film B and superior to tear properties of Comp Film C.

5 In Figure 3, it would be preferred to have the tensile elongation at break as high as possible, to maximize the integrity of the seal area in particular but also the pouch as a whole. Only the 8 mol% sample showed elongation (552%) similar to the films made from commercially available polymers. The films made from Example 3 would be the more preferred composition for a film
10 compared to the composition defined by Example 2.

 The ethylene styrene polymers defined by Examples 2 and 3 have superior stiffness to Comp Film C. In Figure 3, the stiffness of the ethylene styrene films has been shown in terms of the 2% secant modulus. In the preferred melting range of 100°C to 110°C (for low heat seal initiation with good
15 toughness) the ethylene styrene copolymers have 2% secant modulus values of 15000 to 27000 psi. Those values are 2 to 4 times higher than the 6600 psi secant modulus measured on Comp Film C that had a melting point of 102°C. This substantial improvement in stiffness over Comp film C, permits
20 downgauging and easier processing on high speed filling machines with ethylene styrene compositions of Examples 2 and 3.

 Those skilled in the art will recognize that many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

CLAIMS

1. A heat sealable multilayer film for use in manufacturing pouches for containing flowable materials wherein the pouches are in tubular form and have transversely heat sealed ends, said film comprising at least one layer comprising about 10% by volume of the overall film structure and is made from an ethylene-styrene copolymer obtained using a single site catalyst polymerization process and one or more of the following layers:

(a) at least one interpolymer selected from interpolymers of ethylene and one or more C3 - C20 α -olefins made by polymerization processes using single-site catalyst, non-single-site catalyst and mixtures of such catalysts, and blends thereof, said interpolymers having a density in the range of about 0.87 to about 0.940 gm/cc and a melt index of from about 0.2 to about 20 dg/minute and comprising about 10 to about 90% by volume of the overall film structure;

(b) at least one barrier layer selected from nylon polymers comprising about 5 to about 30% by volume of the overall film structure; polyethylene terephthalate polymers comprising about 5 to about 15% by volume of the overall film structure; amorphous nylon comprising about 5 to 30% by volume of the overall structure; ethylene vinyl alcohol comprising about 5 to about 25% by volume of the overall film structure;

(c) at least one tie layer comprising about 5 to about 15% by volume of the overall film structure and selected from ethylene vinyl acetate polymer, ethylene acid copolymers, ionomers or anhydride functionalized ethylene copolymers; and

(d) at least one high pressure ethylene homopolymer.

2. A multilayer film as claimed in Claim 1 wherein the ethylene/styrene copolymer comprises up to about 40 weight percent styrene, has a density range of about 0.93 to about 1.0 g/cm³; a melt index of about 0.3 to about 4 gm/10 min at 190°C; and a molecular weight distribution of Mw/Mn about 2.0 to about 4.0.

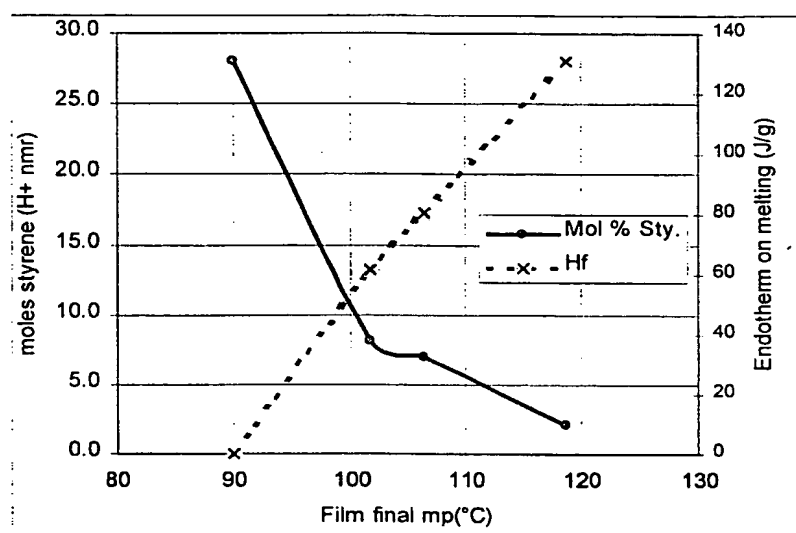
3. A multilayer film as claimed in Claim 1 comprising at least one sealant layer of a copolymer of ethylene and styrene obtained using a single-site catalyst polymerization process.
4. A multilayer film as claimed in Claim 1 wherein the ethylene/styrene copolymer layer has a thickness of from about 25 to about 125 microns thick.
5. A multilayer film as claimed in Claim 1 having a layer structure comprising A/B/A layers, where each A layer is an ethylene/styrene copolymer layer and comprises at least 10% by volume of the overall film structure and B is selected from (a) to (d), and comprises about 50% to about 80% by volume of the overall film structure.
6. A multilayer film as claimed in Claim 1 having a layer structure comprising A/B/C/B/A layers wherein layer A is an ethylene/styrene copolymer and comprises at least about 10% by volume of the overall film structure; C is selected from (a), (b) and (d) and comprises about 5% to about 70% by volume of the overall film structure; and B is a co-extrudable adhesive having a thickness comprising about 5 to about 15% by volume of the overall film structure.
7. A multilayer film as claimed in Claim 1 wherein the ethylene/styrene copolymer multilayer film is laminated, blended or co-extruded with the other layers of the multilayer film.
8. A pouch for containing a flowable material comprising a multilayer film as claimed in anyone of Claims 1 to 7, which pouch is in tubular form and has transversely heat sealed ends.
9. A pouch as claimed in Claim 8 in the shape of a pillow or a self-standing pouch.
10. A process for making pouches filled with a flowable material, using a vertical form, fill and seal apparatus, in which process each pouch is made from a flat web of film by forming a tubular film therefrom with a longitudinal seal and subsequently flattening the tubular film at a first position and transversely heat sealing said tubular film at the flattened position, filling the tubular film with a predetermined quantity of flowable material above said first position,

flattening the tubular film above the predetermined quantity of flowable material at a second position and transversely heat sealing said tubular film at the second position, the improvement comprising making the pouches from a flat web of film comprising a multilayer film as claimed in anyone of Claims 1 to 7.

11. A process as claimed in Claim 10 wherein impulse sealing is used for the transverse heat seals.

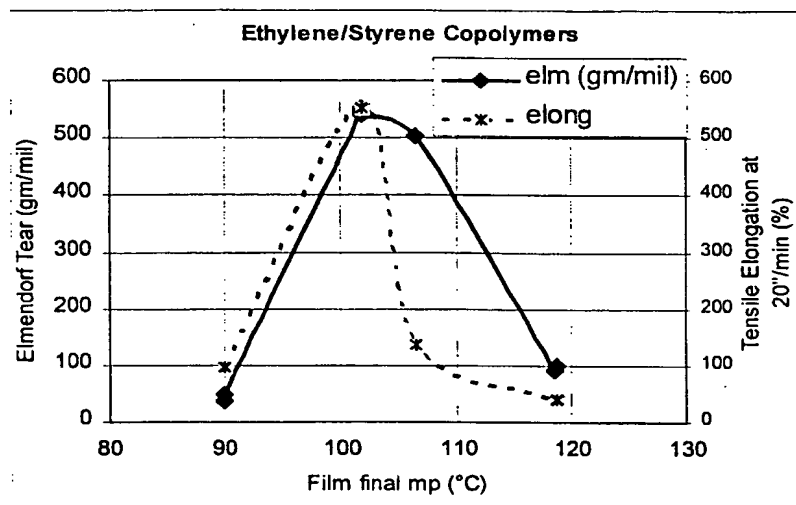
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Figure 1



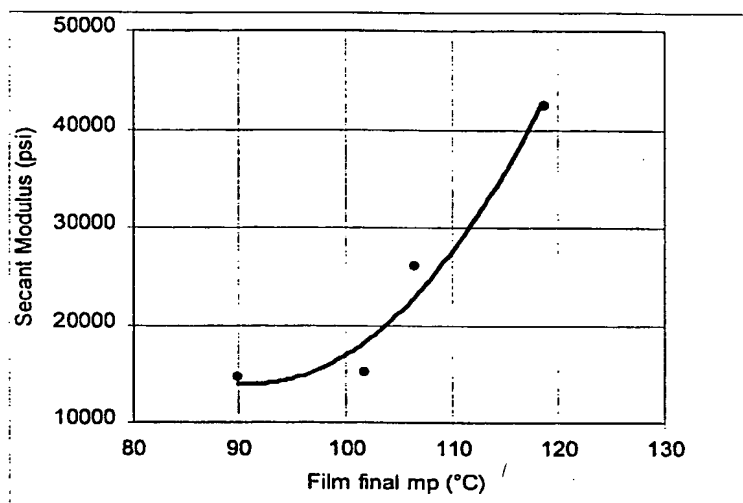
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Figure 2



3/3

Figure 3



INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 98/00424

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B32B27/32 C08L23/08 C09J123/08 B65D65/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	WO 95 32095 A (GRACE W R & CO ;BRADFUTE JOHN G (US); CHILDRESS BLAINE C (US); HAV) 30 November 1995 see examples 28-30,32,33	1-11
P,X	& US 5 658 625 A (BRADFUTE ET AL.) 19 August 1997 cited in the application	1-11
A	WO 95 00333 A (AMERICAN NATIONAL CAN CO) 5 January 1995 see page 11, line 12 - last line see page 7, line 14 - line 26	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

15 July 1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In national Application No

PCT/CA 98/00424

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